

BI  
filling said tank with a fluid comprising water, ozone and an additive acting as a scavenger, and wherein the proportion of said additive in said fluid is less than .5% molar weight of said fluid.

### REMARKS

In paragraph three of the Office Action, claims 27-28 were rejected under 35 U.S.C. §103(a) as being unpatentable over Sakon et al. (U.S. Patent No. 5,560,857) in view of Stanford et al. (U.S. Patent No. 5,244,000) and Kern (Hand Book of Semiconductor wafer cleaning technology) and further in view of Sehested et al. (J.Phys.Chem.).

In one aspect, the current invention discloses a process wherein ozone in combination with a scavenger removes organic contamination on a substrate. Applicants do not believe that the references alone, or taken in combination, render the claims obvious for at least three reasons.

First, the invention is directed to the removal of organic contaminants resulting from a previous lithographic step rather than directed to the removal of metallic contaminants (which is the subject of the Sakon reference). As discussed in paragraph 4 of the enclosed Declaration of Stefan DeGendt which was submitted for Application Serial No. 09/022,834, one of the inventors of the present application, there is a substantial difference between the removal of organic contaminants (and especially the removal of organic contaminants resulting from a previous lithographic step) and the removal of metallic contaminants.

As discussed in paragraph 5 of the enclosed declaration, a typical wet cleaning sequence is SC1 step and then SC2 step. The SC1 step is typically an alkaline oxidizing step, used to

remove particles in general, but is prone to introducing metallic contamination, requiring a further process step (e.g., SC2 step). The SC2 step is typically an acid oxidizing step, used to remove metallic species. The cleaning from the SC1 and SC2 steps is surface (monolayer) cleaning. This cleaning sequence is generally known as an RCA clean and has been introduced by Werner Kern 'RCA Rev. 31, 1970, p.187.

When thicker (visible) layers or residues must be removed, such as a layer of organic photoresist, at least extra processing steps are added. Typically, the sequence is as follows: SPM (sulphuric peroxide mixture) step, then diluted HF step, then SC1 step, and then SC2 step. SPM is a very oxidizing substance which very aggressively removes organic contaminants (such as those caused by a previous lithographic step). The SPM step is typically followed by a step in which diluted HF is applied. After the diluted HF step, the SC1 and SC2 steps are applied to further clean the substrate. The claims currently pending give an alternative to the SPM step. As discussed in the background section of the patent, the SPM step has several disadvantages including: (1) using expensive chemicals; (2) requiring high processing temperatures; and (3) causing serious problems in terms of chemical waste treatment of the sulphuric peroxide mixture. Thus, the present invention avoids the need for using, for example, the caustic substance of the sulphuric peroxide mixture. Instead, a much more environmentally friendly liquid comprised of water, ozone and an additive acting as a scavenger is used, as claimed in claim 27. See paragraph 8 of Declaration of Stefan DeGendt.

The prior art actually teaches away from the use an SC2 step in a photoresist removal step. For example, the appended article by Werner Kern entitled "The Evolution of Silicon

Wafer Cleaning Technology," *J. Electrochem. Soc.*, Vol. 137, June 1990, discusses SC1 and SC2 steps. In the second full paragraph on page 1888, Mr. Kern describes an SC1 step, as shown in the following excerpt:

In the first treatment step, the wafers are exposed to a hop mixture of water-diluted hydrogen peroxide and ammonium hydroxide. This procedure was designed to remove organic surface films by oxidative breakdown and dissolution to expose the silicon or oxide surface for concurrent or subsequent decontamination reactions.

Mr. Kern, again on page 1888, third full paragraph, describes an SC2 step, as shown in the following excerpt:

The second treatment step exposes the rinsed wafer to a hot mixture of water-diluted hydrogen peroxide and hydrochloric acid. This procedure was designed to remove alkali ions and cations such as  $Al^{+3}$ ,  $Fe^{+3}$ , and  $Mg^{+2}$ , that form  $NH_4OH$ -insoluble hydroxides in basic solutions.

On page 1888, in the paragraph beginning with "optional processing steps," a preliminary clean-up treatment with a hot SPM is mentioned, as discussed in the following excerpt:

A preliminary clean-up treatment with a hot  $H_2SO_4$ - $H_2O_2$  mixture (2:1 vol) can be used advantageously for grossly contaminated wafers having visible residues, such as photoresist layers.

Mr. Kern concludes that the chemistry of an SC2 step is not for photoresist removal, as discussed on page 1888 (bottom left paragraph):

However, using high-purity and point-of-use ultrafiltered and particle-free HF solution is used under controlled conditions, more harm than good can result. A silicon surface that was exposed to HF is highly reactive and immediately attracts particles and organic contaminants from solution, DI water, and ambient air. Contrary to SC-1, the subsequent SC-2 solution, which has no surfactant activity, will not eliminate these contaminants.

(Emphasis added). Stefan DeGendt, in his declaration, concludes that not every mixture of an inorganic acid (e.g. HCl) and hydrogen peroxide are capable of removing organic contaminants

from silicon substrates. *See* paragraph 7 of Declaration of Stefan DeGendt. Thus, the Kern reference on page 1888 clearly states that the SC2 step will not affect the removal of photoresist.

Second, the invention calls for the use of ozone rather than the use of hydrogen peroxide (as taught in the Sakon reference). Contrary to the assertion by the Examiner, ozone is not interchangeable with hydrogen peroxide. As an initial matter, ozone is much more environmentally friendly than hydrogen peroxide. *See* paragraph 9 of Declaration of Stefan DeGendt. Moreover, the reactivity of ozone is much higher than hydrogen peroxide. Specifically, in order to provide the necessary reactivity in a hydrogen peroxide mixture, the concentration of the hydrogen peroxide is typically greater than 10% whereas for the equivalent reactivity in an ozone mixture, the concentration of ozone is in the parts per million (ppm) range. *Id.* Finally, ozone is much cheaper to use than hydrogen peroxide. As discussed previously, the concentration of hydrogen peroxide must be above a certain percentage in order to achieve the desired reactivity. Over time, use of the bath decreases the concentration of the hydrogen peroxide, requiring the replacement of the bath or the addition of hydrogen peroxide. By contrast, ozone need only be bubbled up in the mixture, making processing significantly easier. *Id.*

Third, Sakon discloses the use of acetic acid but for an entirely different purpose – not for use as a scavenger, as recited in each of the claims. The Examiner states that the Sakon reference must only teach that the use of acetic acid provides some advantage in the cleaning composition. Applicants respectfully disagree. A general teaching regarding the benefit of using acetic acid, without more, is an insufficient teaching to those skilled in the art to use acetic acid as a

scavenger. Rather, there must be some suggestion to use acetic acid as a scavenger. Clearly, the Sakon reference provides no such teaching and therefore does not render the claims obvious.

In paragraph 3, the Office Action repeated the rejections in paragraphs 8 and 9 of the previous Office Action. Paragraph eight of the previous Office Action rejected claims 29-33 under 35 U.S.C. §103(a) as being unpatentable over Ohmi et al. ("Native Oxide Growth and Organic Impurity Removal on Si Surface with Ozone-Injected Ultrapure Water") in view of Heyns et al. ("New Wet Cleaning Strategies For Obtaining Highly Reliable Thin Oxide"). Paragraph nine of the previous Office Action rejected claims 29 and 34-35 under 35 U.S.C. §103(a) as being unpatentable over Heyns et al. in view of Sakon et al. and further in view of Sehested et al. (J.Phys.Chem.). Neither the Heyns nor the Sakon reference disclose, or even suggest, the use of an additive acting as a scavenger in combination with ozone. As detailed above, this renders the claimed invention novel over the cited art. Moreover, the Sakon reference uses hydrogen peroxide, instead of ozone, which likewise renders the claimed invention novel over the cited art. Thus, Applicants do not believe that the reference alone, or taken in combination, render the claims as written obvious.

In paragraph five of the Office Action, claim 27 was provisionally rejected under 35 U.S.C. §101. Applicants hereby amend claim 27.

In paragraphs seven and eight of the Office Action, claim 27-28 were provisionally rejected under judicially created doctrine of obvious-type double patenting. Upon allowance of claims in the present cases, applicants will submit a terminal disclaimer.

**CONCLUSION**

If for any reason, the application is not considered to be in condition for allowance on the next Office Action and an interview would be helpful to resolve any remaining issues, the Examiner is requested to contact the undersigned attorney at (312) 913-0001.

Respectfully submitted,

**McDonnell Boehnen Hulbert & Berghoff**

Dated: 8/27/01

By: 

Amir N. Penn  
Reg. No. 40,767  
Attorney for Applicant

## APPENDIX UNDER 37 CFR 1.121(c)

27. (Amended) A method for removing organic contaminants from a substrate, the organic contaminants resulting from a previous lithographic step, the method comprising the steps of:

holding said substrate in a tank; and

filling said tank with a fluid comprising water, ozone and an additive acting as a scavenger, and wherein [the fluid is comprised substantially of water] the proportion of said additive in said fluid is less than .5% molar weight of said fluid.